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APPLICATION FOR LETTERS PATENT

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**Semiconductor Processing Methods Of Chemical
Vapor Depositing SiO₂ On A Substrate**

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INVENTOR

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TECHNICAL FIELD

2 This invention relates to semiconductor processing methods of
3 chemical vapor depositing SiO_2 on a substrate.

5 BACKGROUND OF THE INVENTION

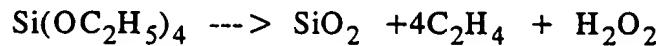
6 Chemical vapor deposited (CVD) SiO_2 films and their binary and
7 ternary silicates find wide use in VLSI processing. These materials find
8 use as insulators between polysilicon and metal layers, between metal
9 layers in multilevel metal systems, as diffusion sources, as diffusion and
10 implantation masks, as capping layers to prevent outdiffusion, and as
11 final passivation layers.

12 The manner in which a thin film covers or conforms to the
13 underlying features on a substrate is an important characteristic in
14 semiconductor processing. Conformal coverage refers to coverage in
15 which equal film thickness exists over all substrate topography regardless
16 of its slope, i.e. vertical and horizontal substrate surfaces are coated
17 with equal film thickness.

18 One manner of effecting the deposition of SiO_2 on a substrate
19 is through pyrolysis of an organic silicon precursor in a CVD reactor
20 to form SiO_2 . A typical organic silicon precursor is tetraethoxysilane
21 or TEOS which is represented by the chemical formula $\text{Si}(\text{OC}_2\text{H}_5)_4$.
22 A typical reactor used to effect the pyrolysis of organic silicon
23 precursors is a low pressure CVD reactor or LPCVD reactor. LPCVD

1 reactors include both hot wall and cold wall reactors. In hot wall
2 reactors, wafers can be heated utilizing radiant heat supplied from
3 resistance-heated coils. In cold wall reactors, wafers can be heated
4 utilizing infrared lamps or rf induction.

5 LPCVD reactors are typically operated at pressures of around
6 0.25-2.0 Torr and temperatures of around 550° C to 800° C, although
7 such parameters may vary depending on a number of different
8 conditions including the particular types of reactants used. The
9 stoichiometry of decomposition of TEOS within an LPCVD reactor may
10 be simplistically written as:



12 Typically, however, intermediates are formed in the above reaction
13 which include di-ethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_3\text{OH}$) and tri-ethoxysilane
14 ($\text{Si}(\text{OC}_2\text{H}_5)_2(\text{OH})_2$). Further, other reaction by-products are formed.

15 One problem facing the semiconductor wafer processor is achieving
16 adequate and conformal step coverage of deposited SiO_2 into very deep
17 and narrow contact openings or other so-called high aspect ratio
18 topographies. One such substrate surface topography is depicted in
19 Figs. 1 and 2 and designated generally by reference numeral 10.
20 Topography 10 is defined by a deep trench 12 into which an SiO_2 layer
21 14 has been deposited as by CVD of a suitable organic silicon
22 precursor such as TEOS.

1 Fig. 1 illustrates a situation in which adequate conformality has
2 been achieved as evidenced by the uniformity or substantial uniformity
3 in thickness of layer 14 over the substrate surface, and particularly
4 within trench 12. Fig. 2 illustrates a situation in which inadequate
5 conformality has resulted in non-uniformity in the thickness of layer 14,
6 particularly at and near the bottom of trench 12. Such is an
7 undesirable condition.

8 One source of inadequate conformality of SiO_2 on a substrate
9 surface is premature formation of undesirable intermediates which react
10 to form SiO_2 at higher topographical elevations on a substrate surface.
11 Consequently, such intermediates never reach the bottom of a particular
12 substrate feature, such as trench 12 of Fig. 2, so that lesser degrees of
13 SiO_2 are formed thereon.

14 One method to improve step coverage has been to increase
15 pressures in the CVD reactor. By doing so, the partial pressure of the
16 organic silicon precursor, such as TEOS, is increased, while the partial
17 pressure of the intermediates is not. The increase in organic silicon
18 precursor partial pressure results in improved step coverage because the
19 precursor has a more favorable sticking coefficient as compared with
20 the intermediates.

21 Another attempt to increase step coverage has been to introduce
22 ethylene (C_2H_4) into the reactor with the precursor to inhibit the
23 premature formation of intermediates. Unfortunately, great success has
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1 not been achieved due to significant degradation of deposition rates
2 stemming from competitive absorption relative to the substrate surface
3 as between the ethylene and the precursor.

4 This invention grew out of the need to provide improved step
5 coverage of LPCVD SiO_2 over high aspect ratio substrate topography.

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7 **SUMMARY OF THE INVENTION**

8 The invention provides semiconductor processing methods of
9 depositing SiO_2 on a substrate.

10 In a preferred aspect, the invention provides methods of reducing
11 the formation of undesired reaction intermediates in a chemical vapor
12 deposition (CVD) decomposition reaction. In one implementation, the
13 method is performed by feeding at least one of H_2O and H_2O_2 into
14 a reactor with an organic silicon precursor. For example, in one
15 exemplary implementation, such components are, in gaseous form, fed
16 separately into the reactor. In another exemplary implementation, such
17 components are combined in liquid form prior to introduction into the
18 reactor, and thereafter rendered into a gaseous form for provision into
19 the reactor. The invention can be practiced with or in both hot wall
20 and cold wall CVD systems.

1 **BRIEF DESCRIPTION OF THE DRAWINGS**

2 Preferred embodiments of the invention are described below with
3 reference to the following accompanying drawings.

4 Fig. 1 illustrates a so-called high aspect ratio semiconductor
5 topography in the form of a trench into which silicon dioxide has been
6 deposited achieving adequate conformal coverage.

7 Fig. 2 illustrates a high aspect ratio semiconductor topography
8 similar to Fig. 1, only one in which inadequate conformal coverage has
9 been achieved.

10 Fig. 3 is a schematic diagram of a chemical vapor deposition
11 system which may be used in conjunction with one preferred aspect of
12 the invention.

13 Fig. 4 is a schematic diagram of a chemical vapor deposition
14 system which may be used in conjunction with another preferred aspect
15 of the invention.

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1 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 This disclosure of the invention is submitted in furtherance of the
3 constitutional purposes of the U.S. Patent Laws "to promote the
4 progress of science and useful arts" (Article 1, Section 8).

5 In accordance with one aspect of the invention, a semiconductor
6 processing method of chemical vapor depositing SiO_2 on a substrate
7 comprises:

8 placing a substrate within a chemical vapor deposition reactor;

9 feeding an organic silicon precursor into the chemical vapor
10 deposition reactor having the substrate positioned therein under
11 conditions effective to decompose the precursor into SiO_2 which deposits
12 on the substrate and into a gaseous oxide of hydrogen; and

13 feeding an additional quantity of the gaseous oxide of hydrogen
14 into the reactor while feeding the organic silicon precursor to the
15 reactor.

16 In accordance with another aspect of the invention, a
17 semiconductor processing method of reducing the decomposition rate of
18 an organic silicon precursor in a chemical vapor deposition process of
19 depositing SiO_2 on a substrate within a chemical vapor deposition
20 reactor comprises feeding at least one of H_2O and H_2O_2 into the
21 reactor while feeding the organic silicon precursor.

1 In accordance with another aspect of the invention, a
2 semiconductor processing method of chemical vapor depositing SiO_2 on
3 a substrate comprises:

4 placing a substrate within a chemical vapor deposition reactor; and
5 feeding an organic silicon precursor and feeding an oxide of
6 hydrogen into the chemical vapor deposition reactor having the substrate
7 positioned therein under conditions effective to deposit an SiO_2 layer
8 on the substrate.

9 In accordance with another aspect of the invention, a
10 semiconductor processing method of reducing the formation of undesired
11 reaction intermediates in a chemical vapor deposition decomposition
12 reaction of an organic silicon precursor into silicon dioxide within a
13 chemical vapor deposition reactor comprises feeding at least one of H_2O
14 and H_2O_2 into the reactor with the organic silicon precursor.

15 Figs. 3 and 4 show schematic diagrams of a different chemical
16 vapor deposition (CVD) systems both of which are designated at 16.
17 The preferred semiconductor processing methods may be carried out in
18 either system in accordance with the description below. The system of
19 Fig. 3 is configured slightly differently from the system of Fig. 4 as will
20 become apparent below. Preferably, CVD systems 16 are low pressure
21 chemical vapor deposition (LPCVD) hot wall systems, although other
22 CVD systems, such as cold wall systems can be used as will become
23 apparent. The illustrated and preferred hot wall systems 16 include a

1 CVD reactor 18 which is configured to carry out depositions at
2 temperatures between around 640° C to 900° C, and at pressures
3 between 100 mTorr to 3 Torr. Various gases can be supplied to
4 reactor 18 from one or more gas sources or bubblers, such as those
5 shown at 20. Such gas sources or bubblers typically hold or contain
6 a liquid mixture which is heated to produce a gas. Such gas from gas
7 sources 20 enters CVD reactor 18 where exposure to temperature and
8 pressure conditions effect deposition of a material, preferably SiO₂, on
9 a semiconductor or wafer substrate therewithin. More than one gas
10 source (Fig. 4) may be used. Inside of CVD reactor 18, a
11 semiconductor wafer holder 22 is provided for holding a plurality of
12 semiconductor wafers or substrates 24. After suitable deposition has
13 occurred, gaseous by-products are exhausted, together with unused
14 reactant and/or diluent gases through exhaust port 26. Reactant gases
15 may be carried by inert diluent or carrier gases such as H₂, N₂ or Ar.

16 Fig. 3 shows system 16 configured for carrying out one preferred
17 semiconductor processing method of chemical vapor depositing SiO₂ on
18 a substrate. Accordingly, system 16 includes a gas source 28. An
19 example of a suitable gas source is a bubbler which contains liquid
20 reactants which are subsequently converted into a gas for provision into
21 a reactor, such as reactor 18. The illustrated and preferred method
22 includes placing a substrate or substrates, such as those shown at 24,
23 within a chemical vapor deposition reactor, such as reactor 18.

1 Reactants which are held in gas source 28 are then heated to produce
2 a gas which is supplied to reactor 18 for further processing in
3 accordance this method. One such reactant is a suitable organic silicon
4 precursor which is preferably tetraethoxysilane or TEOS. Such precursor
5 is fed into reactor 18 wherein substrate 24 is positioned under
6 processing conditions, such as the temperature and pressure conditions
7 mentioned above, which are effective to decompose the precursor into
8 SiO_2 . Although the preferred methods are described as utilizing TEOS
9 as the preferred organic silicon precursor, other such organic silicon
10 precursors may be used. Other precursors include silane, diethylsilane
11 (DES), tetramethylcyclo-tetrasiloxane (TMCTS), fluorotriethoxysilane
12 (FTES), and fluorotrialkoxysilane (FTAS). The SiO_2 deposits on
13 substrates 24 and preferably into high-aspect topography features such
14 as trench 12 in Fig. 1. The organic silicon precursor also decomposes
15 into a gaseous oxide of hydrogen such as H_2O and H_2O_2 . According
16 to a preferred aspect of the invented method, another reactant,
17 preferably either H_2O or H_2O_2 , is provided in liquid form in gas source
18 28. Such additional quantity of the oxide of hydrogen is fed into
19 reactor 18 in gaseous form, while feeding the organic silicon precursor
20 into the reactor. The presence of the additional quantity of the
21 gaseous oxide of hydrogen shifts the reaction equilibrium in the
22 direction of the reactants, thus increasing the partial pressure of the
23 organic silicon precursor. Such inhibits or reduces premature formation
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1 of undesirable intermediates which heretofore have reduced the
2 conformality of the deposition process.

3 Referring still to Fig. 3, quantities of TEOS and the additional
4 quantity of the oxide of hydrogen, both in liquid form, are mixed
5 together to form a liquid mixture. The liquid mixture formed thereby
6 is then converted to a gaseous mixture which is thereafter fed into
7 reactor 18. By first combining liquid forms of the oxide of hydrogen
8 and the organic silicon precursor, and then feeding the gaseous mixture
9 produced thereafter into the reactor, the organic silicon precursor and
10 the additional gaseous quantity of the oxide of hydrogen are fed into
11 the reactor together. Preferably, the quantity of organic silicon
12 precursor, in this example TEOS, in the liquid mixture is greater by
13 volume than the quantity of the oxide of hydrogen. Even more
14 preferably, the liquid mixture volume comprises between about 5% to
15 15% of the oxide of hydrogen. Volumes of the oxide of hydrogen less
16 than about 5% can be utilized to achieve the above-described
17 advantages. Volumes of about 0.5% or lower of either of the oxides
18 of hydrogen may also be utilized. Conversion of the liquid mixture to
19 the gaseous mixture preferably takes place at bubbler temperatures
20 between about 65° to 80°C with a preferred temperature of about 75°C.
21 Thereafter, the gaseous mixture is fed into reactor 18 where it is
22 reacted to deposit SiO₂ on substrates 24 therewithin.

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1 The above described method is one in which the organic silicon
2 precursor and the oxide of hydrogen are first mixed in liquid form to
3 form a liquid mixture. The liquid mixture is then subjected to
4 conditions effective to convert it into a gas which is thereafter fed into
5 the illustrated and preferred hot wall CVD reactor for subsequent
6 deposition processing at temperatures between around 640°C to 900°C.
7 The gaseous mixture is fed into the reactor from a common feed
8 stream.

9 The above described method can also be employed in cold wall
10 LPCVD systems under the following preferred pressure, temperature and
11 other relevant operating conditions. Cold wall deposition conditions or
12 parameters include pressure conditions of around 10 Torr up to an
13 upper limit of around 80 Torr. A preferred temperature for cold wall
14 processing is around 400°C with rf plasma power at 600W. Further, in
15 accordance with this aspect of the invention, O₂ and He flows
16 respectively, are at 600 sccm and 775 sccm. The preferred organic
17 precursor is TEOS which is delivered by liquid injection at 975 sccm.
18 Additionally, a wafer gap to susceptor is around 230 mils. Under the
19 above conditions, a resulting SiO₂ deposition rate of around 7000
20 Angstroms/min is possible.

21 Fig. 4 illustrates schematically a CVD system in which two gas
22 sources or bubblers 30, 32 are shown. Preferably, one of the gas
23 sources contains the organic silicon precursor, preferably TEOS, and the

1 other gas source contains the additional quantity of the oxide of
2 hydrogen, either of H_2O and/or H_2O_2 . In such system, reactor 18 is
3 separately fed with such gaseous reactants. A preferred concentration
4 of gaseous material provided into reactor 18 comprises less than
5 about 50% by volume of the H_2O and/or H_2O_2 . Even more preferably,
6 the volume of material injected into the reactor comprises between
7 about 5% to 15% by volume of the H_2O and/or H_2O_2 . Quantities of
8 H_2O and H_2O_2 less than about 5% of the volume of material injected
9 into the reactor may be utilized to achieve the above-described
10 advantages. Volumes of about 0.5% or lower of either of the oxides
11 of hydrogen can reduce the decomposition rate of the organic silicon
12 precursor sufficiently to allow CVD depositing of SiO_2 on a silicon
13 substrate.

14 The above described method is one in which the reactants are
15 provided in separate bubblers or gas sources, and subjected to
16 conditions effective to convert each to a separate gas. Each separate
17 gas is then separately fed into the reactor and exposed to temperature
18 and pressure conditions effective to deposit an SiO_2 layer on the wafers
19 or substrates held therewithin. The gaseous mixtures are fed into the
20 reactor from separate feed streams. As in the first-described method,
21 the above described method may be utilized in cold wall LPCVD
22 systems under conditions which are the same as or similar to those
23 mentioned above.

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1 In compliance with the statute, the invention has been described
2 in language more or less specific as to structural and methodical
3 features. It is to be understood, however, that the invention is not
4 limited to the specific features shown and described, since the means
5 herein disclosed comprise preferred forms of putting the invention into
6 effect. The invention is, therefore, claimed in any of its forms or
7 modifications within the proper scope of the appended claims
8 appropriately interpreted in accordance with the doctrine of equivalents.

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